

Multicomponent Diffusion in Nanosystems

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(Dated: January 21, 2013)

Abstract

We present the detailed analysis of the diffusive transport of spatially inhomogeneous fluid mixtures and the interplay between structural and dynamical properties varying on the atomic scale. The present treatment is based on different areas of liquid state theory, namely kinetic and density functional theory and their implementation as an effective numerical method via the Lattice Boltzmann approach. By combining the first two methods it is possible to obtain a closed set of kinetic equations for the singlet phase space distribution functions of each species. The interactions among particles are considered within a self-consistent approximation and the resulting effective molecular fields are analyzed. We focus on multispecies diffusion in systems with short-range hard-core repulsion between particles of unequal sizes and weak attractive long-range interactions. As a result, the attractive part of the potential does not contribute explicitly to viscosity but to diffusivity and the thermodynamic properties. Finally, we obtain a practical scheme to solve the kinetic equations by employing a discretization procedure derived from the Lattice Boltzmann approach. Within this framework, we present numerical data concerning the mutual diffusion properties both in the case of a quiescent bulk fluid and shear flow inducing Taylor dispersion.

PACS numbers:

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I. INTRODUCTION

Modern applications in science, medicine and technology require a better understanding of the molecular mechanisms controlling the flow of liquids near solid substrates and at interfaces [1–4]. It is well known that structural and transport properties of highly confined fluids or near free surfaces differ from their bulk behavior due to the large surface to volume ratio [5]. Many phenomena occurring at molecular scales such as diffusion, mixing, shear thinning and lane formation involve the interplay between microscopic structural and transport properties, which need the investigation of the long-time flow behavior. This task is computationally very demanding for approaches such as Molecular Dynamics, so that alternative methods are desirable. Some of these alternative approaches are intermediate between macroscopic thermodynamic and truly microscopic methods and have the scope to incorporate molecular details, at the price of a limited amount of numerical effort. Among these, the dynamic density functional theory (DDFT) and Direct Simulation Monte Carlo (DSMC) are prominent numerical methods. DSMC is a direct particle simulation method based on kinetic theory and its basic idea is to follow the trajectories of a large number of statistically representative particles and stochastic collisions are modeled using scattering probabilities. It gives results which are accurate on scales shorter than the mean free path [11, 12]. The DDFT assumes that the evolution of the system is determined by a “thermodynamic force”, which is the functional derivative of the free energy functional \mathcal{F} with respect the local density [6–10]. In DDFT the state of the solute particles at time t is described by the average density $n(\mathbf{r}, t)$ while the solvent is assimilated to a continuum whose interactions with the solute are modeled via a stochastic heat-bath mechanism. However, this approach is inappropriate to describe the hydrodynamic behavior of simple liquids and liquid mixtures since within the DDFT picture the momentum transport can only occur via diffusion, but not via convection [13–16].

On the contrary, kinetic methods extending the Boltzmann equation to the dense fluid regime, can in principle describe both the thermodynamic and the hydrodynamic behavior of simple fluids. In spite of its great historical relevance in statistical physics, the Boltzmann-Enskog approach has rarely enjoyed the due attention in the area of inhomogeneous fluids, apart from some notable exceptions [17, 18]. The reason perhaps being that, under spatially inhomogeneous conditions, numerical solutions of the equation are impractical. However,

the situation has changed with the advent of modern lattice techniques for solving the Boltzmann equation, collectively named the Lattice Boltzmann Method (LBM) [19–22]. The simultaneous discretization of positional and translational degrees of freedom enables the efficient solution of such an equation by brute force. On the other hand, the application of the LBM to small systems is usually considered to be outside the realm of applicability of kinetic methods, but routinely treated within the DDFT approach, provided that the considered systems are not too far from local equilibrium conditions.

In a series of recent papers we proposed a formulation of the Boltzmann-Enskog theory which is thermodynamically consistent, gives satisfactory values of the transport coefficients, and lends itself to numerical solutions within the LBM framework [23–25]. The method proved to provide reliable results in simple geometrical set-ups and was later extended to multicomponent fluids and to their rich and fascinating phenomenology. In the present paper, we investigate further issues related to the multicomponent system with special attention to the diffusive behavior.

Following few significant studies published on the subject [26–30], but differing from ours in the treatment of the short range correlations, we represent the evolution of the system in terms of the singlet phase space distribution functions, $f^\alpha(\mathbf{r}, \mathbf{v}, t)$, referring to species α . The governing kinetic equations and the balance equations for the density and momentum current of the individual species, obtained in previous work employing the multicomponent extension of the method of Dufty and coworkers [31], are briefly summarized in Sec. II to render the paper self-contained. These balance equations involve different kinds of forces which are the subject of the analysis of Sec. III resulting in an identification of hydrostatic, capillary, viscous and drag forces in terms of microscopic parameters. In Sec. IV we specialize the theory to a binary mixture and in Sec. IV A we turn our attention to the evolution of the local concentration and show how to derive microscopically the advection-diffusion equation under suitable assumptions. In Sec. IV B we perform an hydrodynamic analysis of the coupled set of balance equations in order to illustrate the response of a nearly homogeneous mixture to small deviations from the local equilibrium state. Finally in Sec. V we solve numerically the transport equation utilizing the extension of the Lattice Boltzmann (LBM) method proposed in [25], where the positions are discretized on a lattice and the velocities discretized over a small basis set. This strategy renders the computations efficient and numerically stable. The method was validated against the diffusion of a small periodic inhomogeneity

for several values of the bulk parameters. We have also numerically studied the coupling between microscopic diffusion and a non uniform velocity field, a problem known as Taylor dispersion [32]. A numerical comparison between the analytical work and the numerical solution of the model shows a satisfactory agreement with the theoretical predictions. We conclude this section by discussing the role of the attractive tails in determining the diffusion coefficient. Finally, Sec.VI contains some concluding remarks.

II. MULTICOMPONENT TRANSPORT EQUATION

In the present paper, we shall employ a recent method to describe the isothermal transport properties of a mixture [25]. The idea is to simplify the transport problem by approximating the interaction term in such a way that non-local correlations, giving rise to the microscopic structure of the fluid, are taken into account. The approximation determines a non trivial dependence of the transport coefficients on the density profiles. In a recent paper [25] we have derived the evolution of the singlet phase-space distribution function, $f^\alpha(\mathbf{r}, \mathbf{v}, t)$, characterizing the state of species α , of mass m^α , in a M-component fluid mixture, by means of the following transport equation:

$$\begin{aligned} \frac{\partial}{\partial t} f^\alpha(\mathbf{r}, \mathbf{v}, t) + \mathbf{v} \cdot \nabla f^\alpha(\mathbf{r}, \mathbf{v}, t) + \frac{\mathbf{F}^\alpha(\mathbf{r})}{m^\alpha} \cdot \frac{\partial}{\partial \mathbf{v}} f^\alpha(\mathbf{r}, \mathbf{v}, t) = \\ -\omega[f^\alpha(\mathbf{r}, \mathbf{v}, t) - \psi_\perp^\alpha(\mathbf{r}, \mathbf{v}, t)] + \frac{\Phi^\alpha(\mathbf{r}, t)}{k_B T} \cdot (\mathbf{v} - \mathbf{u}(\mathbf{r}, t)) \psi^\alpha(\mathbf{r}, \mathbf{v}, t), \end{aligned} \quad (1)$$

where \mathbf{F}^α is an external body force acting on species α , T the uniform temperature of the system and k_B the Boltzmann constant. The central quantity of eq. (1) is $\Phi^\alpha(\mathbf{r}, t)$, which bears the result of collisions between particles, and whose details will be given below. In addition, ψ^α is the local Maxwellian equilibrium of specie α ,

$$\psi^\alpha(\mathbf{r}, \mathbf{v}, t) = n^\alpha(\mathbf{r}, t) \left[\frac{m^\alpha}{2\pi k_B T} \right]^{3/2} \exp\left(-\frac{m^\alpha (\mathbf{v} - \mathbf{u}(\mathbf{r}, t))^2}{2k_B T} \right) \quad (2)$$

and the distribution ψ_\perp^α shares to the same average density and velocity as the actual distribution f^α :

$$\psi_\perp^\alpha(\mathbf{r}, \mathbf{v}, t) = \psi^\alpha(\mathbf{r}, \mathbf{v}, t) \left\{ 1 + \frac{m^\alpha (\mathbf{u}^\alpha(\mathbf{r}, t) - \mathbf{u}(\mathbf{r}, t)) \cdot (\mathbf{v} - \mathbf{u}(\mathbf{r}, t))}{k_B T} \right\} \quad (3)$$

Eqs. (1)-(2) contain the fields n^α , \mathbf{u}^α , \mathbf{u} , the average partial number density of the component α , its average velocity and the barycentric velocity of the mixture, respectively. The first two quantities are defined by:

$$\begin{pmatrix} n^\alpha(\mathbf{r}, t) \\ n^\alpha(\mathbf{r}, t)\mathbf{u}^\alpha(\mathbf{r}, t) \end{pmatrix} = \int d\mathbf{v} \begin{pmatrix} 1 \\ \mathbf{v} \end{pmatrix} f^\alpha(\mathbf{r}, \mathbf{v}, t). \quad (4)$$

One also needs to specify the partial mass density, $\rho^\alpha(\mathbf{r}, t) = m^\alpha n^\alpha(\mathbf{r}, t)$, the global number density, $n(\mathbf{r}, t) = \sum_\alpha n^\alpha(\mathbf{r}, t)$, the global mass density

$$\rho(\mathbf{r}, t) = \sum_\alpha \rho^\alpha(\mathbf{r}, t) \quad (5)$$

and the barycentric average velocity at position \mathbf{r} :

$$\mathbf{u}(\mathbf{r}, t) = \frac{\sum_\alpha \rho^\alpha(\mathbf{r}, t)\mathbf{u}^\alpha(\mathbf{r}, t)}{\sum_\alpha \rho^\alpha(\mathbf{r}, t)} \quad (6)$$

Eq. (1) is an approximate isothermal representation of the revised Enskog theory (RET) kinetic equation [33] where, in order to obtain a workable scheme, the non-linear collision operator has been replaced by the two terms featuring in the r.h.s. of the equation. It is a simplified representation of the multicomponent RET for hard sphere mixtures, which contains two features that go beyond the standard Boltzmann equation approach [34]. The colliding particles are separated by a distance equal to the sum of their radii and the collision frequency is modified to take into account the excluded volume effect through the introduction of the pair correlation function at contact in the collision integral. Such a pair correlation function depends on the densities through a smoothing procedure. The first term in the l.h.s. of eq. (1) describes the fast relaxation process towards local equilibrium and represents in an approximate fashion the non-hydrodynamic part of the collision operator. It contains ω , a collision frequency assumed to be the same for all species.

The form of the first term in the r.h.s of eq (1) is clearly reminiscent of the Bhatnagar-Gross-Krook (BGK) relaxation term employed in the treatment of one-component systems [35]. It contains an additional factor making the difference between ψ_\perp^α and ψ^α . The factor multiplying the Maxwellian in eq. (3) serves to "orthogonalize" the term $-\omega[f^\alpha - \psi_\perp^\alpha]$ to the term containing the effective fields, Φ^α , as specified below. Such a modification is necessary in order to produce the correct balance equation for the partial momentum and to obtain the correct form of the momentum equation for the individual components (see eq. (8)).

In the following, we consider the evolution of the partial density and of partial momentum current. The first is obtained by integrating eq. (1) w.r.t. the velocity

$$\frac{\partial}{\partial t}\rho^\alpha(\mathbf{r}, t) + \nabla \cdot \left(\rho^\alpha(\mathbf{r}, t)\mathbf{u}(\mathbf{r}, t) \right) + \nabla \cdot \left(\rho^\alpha(\mathbf{r}, t)(\mathbf{u}^\alpha(\mathbf{r}, t) - \mathbf{u}(\mathbf{r}, t)) \right) = 0, \quad (7)$$

where the last term in eq. (7) is the so-called dissipative diffusion current, measuring the drift of the α -component with respect to the center of mass velocity.

Multiplication of eq. (1) by $m^\alpha \mathbf{v}$ and integration w.r.t. \mathbf{v}^α yields the balance equation for the momentum of the species α :

$$\begin{aligned} \frac{\partial}{\partial t}[\rho^\alpha(\mathbf{r}, t)u_j^\alpha(\mathbf{r}, t)] + \nabla_i \left(\rho^\alpha(\mathbf{r}, t)u_i^\alpha(\mathbf{r}, t)u_j^\alpha(\mathbf{r}, t) - \rho^\alpha(\mathbf{r}, t)(u_i^\alpha(\mathbf{r}, t) - u_i(\mathbf{r}, t))(u_j^\alpha(\mathbf{r}, t) - u_j(\mathbf{r}, t)) \right) = \\ -\nabla_i \pi_{ij}^\alpha(\mathbf{r}, t) + \frac{F_j^\alpha(\mathbf{r})}{m^\alpha} \rho^\alpha(\mathbf{r}, t) + \frac{\Phi_j^\alpha(\mathbf{r}, t)}{m^\alpha} \rho^\alpha(\mathbf{r}, t), \end{aligned} \quad (8)$$

where

$$\pi_{ij}^\alpha(\mathbf{r}, t) = m^\alpha \int d\mathbf{v} (v_i - u_i)(v_j - u_j) f^\alpha(\mathbf{r}, \mathbf{v}, t) \quad (9)$$

represents the kinetic contribution of component α to the pressure tensor. Here and in the following the Einstein convention on repeated indices is employed.

III. FORCE ANALYSIS

In ref. [25] we derived an explicit expression for the effective fields, $\Phi^\alpha(\mathbf{r}, t)$, for a model with repulsive hard sphere potentials of different diameters, $\sigma_{\alpha\alpha}$ and masses m^α , plus long range attractive interactions with associated potential term $U^{\alpha\beta}$. The central notion is that this quantity is a functional of the density and velocity of each species. By treating the repulsive contribution in the framework of the revised Enskog theory [33], and the attractive term within the random phase approximation (RPA) [36], the effective field is represented as a sum of forces of different nature:

$$\Phi^\alpha(\mathbf{r}, t) = \mathbf{F}^{\alpha, mf}(\mathbf{r}, t) + \mathbf{F}^{\alpha, drag}(\mathbf{r}, t) + \mathbf{F}^{\alpha, visc}(\mathbf{r}, t). \quad (10)$$

The first term represents the force acting on species α at position \mathbf{r} due to the influence of all remaining particles in the system, and is the gradient of the so-called potential of mean force. When the system is in thermodynamic equilibrium such a force is related to the excess

of the chemical potential [37, 38] over its ideal gas value, μ_{exc}^α , of the α component by the relation:

$$\mathbf{F}^{\alpha,mf}(\mathbf{r}, t) = -\nabla \mu_{exc}^\alpha(\mathbf{r}, t). \quad (11)$$

Explicitly, using the form of the RET collision term and an attractive potential tail, we obtain the following representation

$$\mathbf{F}^{\alpha,mf}(\mathbf{r}, t) = -k_B T \sum_{\beta} \sigma_{\alpha\beta}^2 \int d\hat{\mathbf{s}} \hat{\mathbf{s}} g_{\alpha\beta}(\mathbf{r}, \mathbf{r} + \sigma_{\alpha\beta} \hat{\mathbf{s}}, t) n_{\beta}(\mathbf{r} + \sigma_{\alpha\beta} \hat{\mathbf{s}}, t) + \sum_{\beta} \mathbf{G}^{\alpha\beta}(\mathbf{r}, t) \quad (12)$$

where $\sigma_{\alpha\beta} = (\sigma_{\alpha\alpha} + \sigma_{\beta\beta})/2$ and the integration in the first term of the r.h.s. is over the unit spherical surface, while the last term represents the molecular fields associated with the attractive forces:

$$\mathbf{G}^{\alpha\beta}(\mathbf{r}, t) = - \int d\mathbf{r}' n^{\beta}(\mathbf{r}', t) g_{\alpha\beta}(\mathbf{r}, \mathbf{r}') \nabla_r U^{\alpha\beta}(\mathbf{r} - \mathbf{r}') \quad (13)$$

The second and third terms of eq. (10) carry a functional dependence on the velocities, contributions that are neglected in semi-macroscopic models of single or multicomponents [39]. These terms are crucial for the correct characterization of dissipation and diffusion in the condensed state and result in density-dependent transport coefficients.

The second term in the r.h.s. of eq. (10) is the drag force exerted by unlike species on the particle α in reason of their different drift velocities:

$$\mathbf{F}^{\alpha,drag}(\mathbf{r}, t) = - \sum_{\beta} \gamma^{\alpha\beta}(\mathbf{r}, t) (\mathbf{u}^{\alpha}(\mathbf{r}, t) - \mathbf{u}^{\beta}(\mathbf{r}, t)), \quad (14)$$

where we have introduced an inhomogeneous friction tensor via the equation:

$$\gamma_{ij}^{\alpha\beta}(\mathbf{r}, t) = 2\sigma_{\alpha\beta}^2 \sqrt{\frac{2\mu_{\alpha\beta} k_B T}{\pi}} \int d\hat{\mathbf{s}} s_i s_j g_{\alpha\beta}(\mathbf{r}, \mathbf{r} + \sigma_{\alpha\beta} \hat{\mathbf{s}}, t) n^{\beta}(\mathbf{r} + \sigma_{\alpha\beta} \hat{\mathbf{s}}, t). \quad (15)$$

Finally, the last term in the r.h.s. of eq. (10) represents the viscous force due to the presence of velocity gradients:

$$\mathbf{F}^{\alpha,visc}(\mathbf{r}, t) = \sum_{\beta} 2\sigma_{\alpha\beta}^2 \sqrt{\frac{2\mu_{\alpha\beta} k_B T}{\pi}} \int d\hat{\mathbf{s}} \hat{\mathbf{s}} g_{\alpha\beta}(\mathbf{r}, \mathbf{r} + \sigma_{\alpha\beta} \hat{\mathbf{s}}, t) n^{\beta}(\mathbf{r} + \sigma_{\alpha\beta} \hat{\mathbf{s}}, t) \hat{\mathbf{s}} \cdot (\mathbf{u}^{\beta}(\mathbf{r} + \sigma_{\alpha\beta} \hat{\mathbf{s}}) - \mathbf{u}^{\beta}(\mathbf{r})), \quad (16)$$

where $g_{\alpha\beta}(\mathbf{r}, \mathbf{r} + \sigma_{\alpha\beta} \hat{\mathbf{s}}, t)$ is the pair correlation functions at contact ($|\mathbf{r} - \mathbf{r}'| = \sigma_{\alpha\beta}$) and $\mu_{\alpha\beta}$ is the reduced mass $\mu_{\alpha\beta} = \frac{m^{\alpha} m^{\beta}}{m^{\alpha} + m^{\beta}}$ for the colliding pair.

In the case of weak spatially periodic deviations from the homogeneous reference state, it is possible to derive explicit expressions for the effective forces discussed above. At first, let us consider a slowly varying periodic variation of the densities of the two species of the form:

$$n^\alpha(\mathbf{r}, t) = n_0^\alpha(t) + \delta n^\alpha(t) e^{i\mathbf{q}\cdot\mathbf{r}} \quad (17)$$

where $q\sigma_{\alpha\beta} \ll 1$ and n_0^α are uniform densities. By substituting such a density profile into eq. (12) and expanding the resulting integrals up to second order in the parameter $q\sigma_{\alpha\beta}$, we find the expression:

$$\mathbf{F}^{\alpha, mf}(\mathbf{r}, t) \simeq -i\mathbf{q} e^{i\mathbf{q}\cdot\mathbf{r}} \sum_{\beta} \delta n^\beta(t) \left[k_B T \frac{4\pi}{3} \left(\sigma_{\alpha\beta}^3 g_{\alpha\beta}^{bulk} + \frac{1}{2} \sum_{\gamma} n^\gamma \sigma_{\alpha\gamma}^3 \frac{\partial g_{\alpha\gamma}^{bulk}}{\partial n^\beta} \right) - w_0^{\alpha\beta} + \frac{1}{2} w_2^{\alpha\beta} q^2 \right] \quad (18)$$

with $w_n^{\alpha\beta} = \int d\mathbf{r} |\mathbf{r}|^n U^{\alpha\beta}(\mathbf{r})$. The last term in the l.h.s. of eq. (18) corresponds to the contribution to the local force acting on the species α stemming from the attractive interactions [38].

Similarly, we estimate the viscous force by considering uniform densities and a weak periodic velocity field $\mathbf{u}(\mathbf{r}, t) = \mathbf{u}(t) e^{i\mathbf{q}\cdot\mathbf{r}}$, with $\mathbf{u}^A = \mathbf{u}^B$. We find

$$\mathbf{F}_{\perp}^{\alpha, visc}(\mathbf{r}, t) \simeq -\frac{4\pi}{15} q^2 \mathbf{u}_{\perp}(t) e^{i\mathbf{q}\cdot\mathbf{r}} \sum_{\beta} \sigma_{\alpha\beta}^4 n_0^\beta g_{\alpha\beta} \sqrt{\frac{2\mu_{AB} k_B T}{\pi}}, \quad (19)$$

and

$$\mathbf{F}_{\parallel}^{\alpha, visc}(\mathbf{r}, t) \simeq -\frac{4\pi}{5} q^2 \mathbf{u}_{\parallel}(t) e^{i\mathbf{q}\cdot\mathbf{r}} \sum_{\beta} \sigma_{\alpha\beta}^4 n_0^\beta g_{\alpha\beta} \sqrt{\frac{2\mu_{AB} k_B T}{\pi}}, \quad (20)$$

where we have considered the parallel and the perpendicular part of the velocity with respect to the wave-vector \mathbf{q} . As a result we obtain

$$\gamma^{\alpha\beta} = \frac{8}{3} \sqrt{2\pi\mu_{\alpha\beta} k_B T} g_{\alpha\beta} n_0^\beta \sigma_{\alpha\beta}^2. \quad (21)$$

IV. THE BINARY MIXTURE

In order to proceed with analytical work it is more convenient to use as variables the local mass density and local momentum variables together with concentration variables. The new equations can be obtained by combining appropriately equations (7) and (8).

By specializing to a binary mixture, AB, the local concentration is defined as

$$c(\mathbf{r}, t) = \frac{\rho^A(\mathbf{r}, t)}{\rho(\mathbf{r}, t)} \quad (22)$$

From the evolution equations (7) for the partial densities, the mass continuity equation reads

$$\partial_t \rho(\mathbf{r}, t) + \nabla \cdot (\rho(\mathbf{r}, t) \mathbf{u}(\mathbf{r}, t)) = 0. \quad (23)$$

and the conservation law for the local concentration

$$\frac{\partial}{\partial t} c(\mathbf{r}, t) + \mathbf{u}(\mathbf{r}, t) \cdot \nabla c(\mathbf{r}, t) + \frac{1}{\rho} \nabla \cdot (\rho(\mathbf{r}, t) c(\mathbf{r}, t) (1 - c(\mathbf{r}, t)) \mathbf{w}(\mathbf{r}, t)) = 0, \quad (24)$$

where we have introduced the velocity difference

$$\mathbf{w}(\mathbf{r}, t) \equiv \mathbf{u}^A(\mathbf{r}, t) - \mathbf{u}^B(\mathbf{r}, t). \quad (25)$$

Using eq.(8), the equation expressing the total momentum balance reads

$$\begin{aligned} \partial_t u_j(\mathbf{r}, t) + u_i(\mathbf{r}, t) \nabla_i u_j(\mathbf{r}, t) + \frac{1}{\rho} \nabla_i \pi_{ij}^{(K)} \\ - \frac{1}{\rho} \left(n^A(\mathbf{r}, t) [F_j^A(\mathbf{r}) + F_j^{A,mf}(\mathbf{r}, t) + F_j^{A,visc}(\mathbf{r}, t)] + n^B(\mathbf{r}, t) [F_j^B(\mathbf{r}) + F_j^{B,mf}(\mathbf{r}, t) + F_j^{B,visc}(\mathbf{r}, t)] \right) = 0. \end{aligned} \quad (26)$$

To proceed further, it is convenient to define the total local chemical potential of each species $A(B)$ through the equation:

$$\nabla_j \mu^{A(B)}(\mathbf{r}, t) \equiv \frac{1}{n^{A(B)}(\mathbf{r}, t)} \nabla_i \pi_{ij}^{A(B)}(\mathbf{r}, t) \delta_{ij} - F_j^{A(B),mf}(\mathbf{r}, t), \quad (27)$$

where we used eq. (11) for the non ideal part and the relation between the ideal gas pressure and the chemical potential of an ideal gas. In the isothermal system, the gradient of the total thermodynamic pressure is defined as

$$\nabla_j P(\mathbf{r}, t) \equiv n^A(\mathbf{r}, t) \nabla_j \mu^A(\mathbf{r}, t) + n^B(\mathbf{r}, t) \nabla_j \mu^B(\mathbf{r}, t) \quad (28)$$

that can be seen as a special case of the Gibbs-Duhem equation.

In the following we shall use the fact that the kinetic contribution to the gradient of the pressure tensor, $\pi_{ij}^{(K)} = \pi_{ij}^A + \pi_{ij}^B$, can be written as:

$$\nabla_i \pi_{ij}^{(K)} \simeq \delta_{ij} \nabla_j P_{id} - \eta^{(K)} \left(\frac{1}{3} \nabla_i \nabla_j u_i + \nabla_i^2 u_j \right), \quad (29)$$

with $P_{id} = k_B T (n^A(\mathbf{r}, t) + n^B(\mathbf{r}, t))$ and $\eta^{(K)} = \frac{k_B T}{\omega} (n^A(\mathbf{r}, t) + n^B(\mathbf{r}, t))$. As shown in Ref. [40], in the limit of small gradients also the non-ideal contribution to the viscous force in the momentum equation can be written as:

$$\sum_{\alpha} n^{\alpha}(\mathbf{r}, t) \mathbf{F}^{\alpha,visc}(\mathbf{r}, t) \simeq -\eta^{(C)} \nabla^2 \mathbf{u} - \left(\frac{1}{3} \eta^{(C)} + \eta_b^{(C)} \right) \nabla (\nabla \cdot \mathbf{u}) \quad (30)$$

where the non-ideal contribution to the shear viscosity is

$$\eta^{(C)} = \frac{4}{15} \sum_{\alpha\beta} \sqrt{2\pi\mu_{\alpha\beta}k_B T} \sigma_{\alpha\beta}^4 g_{\alpha\beta} n_0^\alpha n_0^\beta, \quad (31)$$

while the bulk viscosity is

$$\eta_b^{(C)} = \frac{5}{3} \eta^{(C)}. \quad (32)$$

Notice that, within our approximations the kinetic contribution to the bulk viscosity vanishes: $\eta_b^{(K)} = 0$.

In order to derive an expression for \mathbf{w} , we compute the difference between the velocities of the two components using eq. (8), and derive the following equation :

$$\begin{aligned} & \frac{\partial}{\partial t} w_j(\mathbf{r}, t) + \left[u_i^M(\mathbf{r}, t) \nabla_i w_j(\mathbf{r}, t) + w_i(\mathbf{r}, t) \nabla_i u_j^M(\mathbf{r}, t) \right] \\ & - \frac{1}{\rho^A} \nabla_i \left(\frac{\rho^A (\rho^B)^2}{\rho^2} w_i(\mathbf{r}, t) w_j(\mathbf{r}, t) \right) + \frac{1}{\rho^B} \nabla_i \left(\frac{\rho^B (\rho^A)^2}{\rho^2} w_i(\mathbf{r}, t) w_j(\mathbf{r}, t) \right) \Big] = \\ & - \left(\frac{1}{\rho^A} \nabla_i \pi_{ij}^A - \frac{1}{\rho^B} \nabla_i \pi_{ij}^B \right) + \left(\frac{\Phi_j^A(\mathbf{r}, t) + F_j^A(\mathbf{r})}{m^A} - \frac{\Phi_j^B(\mathbf{r}, t) + F_j^B(\mathbf{r})}{m^B} \right), \end{aligned} \quad (33)$$

with the abbreviation $\mathbf{u}^M \equiv (\mathbf{u}^A + \mathbf{u}^B)/2$. Before studying such an equation we shall make some considerations.

A. Homogeneous diffusion

The phenomenon of multicomponent diffusion has ever since attracted a vivid interest [41–48]. We shall specialize the discussion to the binary mixture and consider first a system where diffusion is the dominant mechanism to restore equilibrium, assuming that the global velocity of the fluid is nearly uniform.

In eq. (8) the inertial term, $\nabla_i[\rho^\alpha u_i^\alpha u_j^\alpha]$, is small with respect to the terms associated with the viscous component of the kinetic and potential parts of the pressure tensor (see eq. (16)), $(\nabla_i \pi_{ij}^\alpha + n^\alpha F_j^{\alpha, visc})$, and their ratio is given by:

$$\frac{\nabla_i[\rho^\alpha u_i^\alpha u_j^\alpha]}{(\nabla_i \pi_{ij}^\alpha + n^\alpha F_j^{\alpha, visc})} \simeq \frac{\rho u^2/L}{\eta u/L^2} = \frac{\rho u L}{\eta} = \mathcal{R}, \quad (34)$$

where L is the typical spatial scale of the gradients, u the velocity of the flow and η the shear viscosity and \mathcal{R} is the Reynolds number. In eq. (33) the viscous term is also negligible

with respect to the chemical potential term :

$$\frac{\eta \nabla^2 u}{n \nabla \mu} \simeq \frac{\eta u / L^2}{\rho c_s^2 L} = \frac{1}{\mathcal{R}} \frac{u^2}{c_s^2} = \frac{Ma^2}{\mathcal{R}} \quad (35)$$

where c_s is the sound velocity and $Ma = u/c_s$ the Mach number. Thus, in the regime of low velocities the ratio (35) is small and the viscous force in eq. (33) can be safely neglected. Using eq. (14), we rewrite eq. (33) as

$$\frac{\partial}{\partial t} w_i(\mathbf{r}, t) + \nabla_i \mu_D(\mathbf{r}, t) + \left(\frac{1}{m^A} \gamma_{ij}^{AB}(\mathbf{r}, t) + \frac{1}{m^B} \gamma_{ij}^{BA}(\mathbf{r}, t) \right) w_j(\mathbf{r}, t) = \left(\frac{F_i^A(\mathbf{r})}{m^A} - \frac{F_i^B(\mathbf{r})}{m^B} \right) \quad (36)$$

where the appropriate thermodynamic field, μ_D , conjugated to the concentration variable, $c = \rho^A/\rho$, is the difference in the chemical potentials per unit mass of the two components [36] defined as:

$$\nabla_j \mu_D(\mathbf{r}, t) \equiv \frac{1}{m^A} \nabla_j \mu^A(\mathbf{r}, t) - \frac{1}{m^B} \nabla_j \mu^B(\mathbf{r}, t). \quad (37)$$

In the homogeneous case the friction tensor is isotropic and diagonal and can be written as

$$\gamma \equiv \frac{1}{m^A} \gamma_{ii}^{AB}(\mathbf{r}, t) + \frac{1}{m^B} \gamma_{ii}^{BA}(\mathbf{r}, t) = \frac{8}{3} \rho \frac{\sqrt{2\pi \mu_{AB} k_B T}}{m^A m^B} g_{AB}^{bulk} \sigma_{AB}^2. \quad (38)$$

It can also be assumed that in eq. (36) the variation in time of \mathbf{w} is slow, so that

$$\mathbf{w}(\mathbf{r}, t) = -\frac{1}{\gamma} \left\{ \nabla \mu_D(\mathbf{r}, t) - \left(\frac{\mathbf{F}^A(\mathbf{r})}{m^A} - \frac{\mathbf{F}^B(\mathbf{r})}{m^B} \right) \right\} \quad (39)$$

Using the Gibbs-Duhem equation, eq.(28), the chemical potential difference can be expressed as

$$\nabla \mu_D = \frac{\rho}{n m^A m^B} \left(\nabla(\mu^A - \mu^B) + (m^B - m^A) \frac{1}{\rho} \nabla P \right) \quad (40)$$

by substituting into eq. (36), we find that in stationary conditions,

$$\mathbf{w}(\mathbf{r}, t) = -\frac{D^{AB}}{k_B T} \left\{ \nabla(\mu^A - \mu^B) + (m^B - m^A) \frac{1}{\rho} \nabla P - \frac{n}{\rho} m^A m^B \left(\frac{\mathbf{F}^A(\mathbf{r})}{m^A} - \frac{\mathbf{F}^B(\mathbf{r})}{m^B} \right) \right\}, \quad (41)$$

where we have introduced the mutual diffusion coefficient D^{AB} (see ref. [43]) through the linear relation between the velocity and the difference between the chemical potential gradients, the factor $(k_B T)^{-1}$ having been introduced in the definition for dimensionality reasons. By comparing eqs. (39) and (41) we find

$$D^{AB} = \frac{k_B T}{\gamma} \frac{\rho}{n m^A m^B}, \quad (42)$$

which in the case of equal masses takes the simpler form $D^{AB} = \frac{k_B T}{\gamma} \frac{1}{m}$. Eq. (43) relates a response quantity, the friction coefficient γ to a fluctuation quantity, D^{AB} , the mutual diffusion coefficient, according to the Einstein relation.

Relation (41) expresses the fact that the diffusion velocity is opposed to the gradient of the concentration field (proportional to the first term within the parenthesis) and that heavier molecules tend to move towards regions of higher pressure. The last term in eq. (41) corresponds to the so-called forced diffusion. We have neglected the Soret effect, that is, the coupling with the temperature gradient, being consistent with our isothermal treatment. The appropriate extension of the present theory to thermal systems was proposed in ref. [40]. Using eq. (38), for γ , the mutual diffusion coefficient can be written explicitly as:

$$D^{AB} = \frac{3}{8n} \frac{(k_B T)^{1/2}}{(2\pi\mu^{AB})^{1/2}(\sigma_{AB})^2 g_{AB}^{bulk}}, \quad (43)$$

an expression identical to that derived from the Enskog analysis [41]. Moreover, assuming that the mass density variations are negligible and using the relation between the chemical potential difference μ_D and the Gibbs free energy per unit mass $G(P, T, n, c)$ [49] ,

$$\left. \frac{\partial G}{\partial c} \right|_{P, T, n} = \mu_D,$$

we can write the advection-diffusion equation for the mass concentration in the suggestive form

$$\frac{\partial}{\partial t} c(\mathbf{r}, t) + \mathbf{u} \cdot \nabla c(\mathbf{r}, t) = \frac{1}{\gamma} \nabla \left[(c(\mathbf{r}, t)(1 - c(\mathbf{r}, t))) \nabla \frac{\delta G[c]}{\delta c(\mathbf{r}, t)} \right] \quad (44)$$

which bears a close resemblance with the typical DDFT equation, with the Gibbs potential per unit mass G replacing the Helmholtz free energy per unit volume. In the case of a binary ideal gas mixture ($g_{\alpha\beta}^{bulk} = 1$) with equal masses, we recover the standard advection-diffusion equation with a constant diffusion coefficient:

$$\frac{\partial}{\partial t} c(\mathbf{r}, t) + \mathbf{u} \cdot \nabla c(\mathbf{r}, t) = D^{AB} \nabla^2 c(\mathbf{r}, t) \quad (45)$$

Notice that the present diffusion coefficient D^{AB} corresponds to the Enskog and not to the Stokes-Einstein expression, since the underlying dynamics is purely markovian [36, 40].

Before concluding this section, we recall that, within the random phase approximation, the presence of attractive tails in the pair potentials does not produce any change on the coefficients of viscosity and thermal conductivity with respect to their values in the hard-sphere system. This result is an artifact of the RPA method and is worse than the corresponding

result obtained via the Enskog method [41]. However, the value of the diffusion coefficient does depend on the potential tails as pointed out in ref. [50]. In fact, the diffusion current is proportional to the gradient of the chemical potential difference μ_D of eq. (37).

In Fig. 1, we display the behavior of the mutual diffusion coefficient for a mixture of equisized hard-spheres as a function of the bulk concentration for three different values of the bulk packing fraction. The relative strength of the attractive tails was fixed empirically according to the geometric mean Lorentz-Berthelot mixing rule [51]:

$$w_{AB} = \sqrt{w_{AA}w_{BB}} \quad (46)$$

and set $w_{AA} = 5k_B T$ and $w_{BB} = w_{AA}/2$.

We observe that the presence of attractive interactions tends to reduce the value of D^{AB} . The largest deviation from the unperturbed value occurs at concentration $c = 1/2$ and decreases at fixed packing fraction as the diameter increases.

B. Hydrodynamic analysis

We now turn our attention to the case where interspecies diffusion is coupled to acoustic and shear modes. The following treatment will be based on linearized equations and has the purpose of connecting the macroscopic hydrodynamic properties, such as the dispersion relations of the propagating modes and their damping, to the microscopic parameters of the underlying model. After linearizing eqs. (23),(24), (26) and (33) around the state $(\rho_0, c_0, \mathbf{u} = 0, \mathbf{w} = 0)$ we find the following set of equations

$$\partial_t \delta \rho(\mathbf{r}, t) + \rho_0 \nabla \cdot \mathbf{u}(\mathbf{r}, t) = 0 \quad (47)$$

$$\partial_t \mathbf{u}(\mathbf{r}, t) + \frac{1}{\rho_0} \nabla P(\mathbf{r}, t) - \frac{1}{\rho_0} \left(\eta \nabla^2 \mathbf{u}(\mathbf{r}, t) + \left(\frac{1}{3} \eta + \eta_b \right) \nabla (\nabla \cdot \mathbf{u}(\mathbf{r}, t)) \right) = 0 \quad (48)$$

$$\frac{\partial}{\partial t} \mathbf{w}(\mathbf{r}, t) + \nabla \mu_D(\mathbf{r}, t) + \gamma \mathbf{w}(\mathbf{r}, t) = 0 \quad (49)$$

$$\partial_t \delta c(\mathbf{r}, t) + c_0(1 - c_0) \nabla \cdot \mathbf{w}(\mathbf{r}, t) = 0. \quad (50)$$

We now insert the trial solutions, with $\delta\rho, \delta c_0, \mathbf{u}_0, \mathbf{w}_0$ constants,

$$\delta\rho(\mathbf{r}, t) = \delta\rho_0 e^{\zeta t + i\mathbf{q}\cdot\mathbf{r}} \quad (51)$$

$$\mathbf{u}(\mathbf{r}, t) = \mathbf{u}_0 e^{\zeta t + i\mathbf{q}\cdot\mathbf{r}} \quad (52)$$

$$\delta c(\mathbf{r}, t) = \delta c_0 e^{\zeta t + i\mathbf{q}\cdot\mathbf{r}} \quad (53)$$

$$\mathbf{w}(\mathbf{r}, t) = \mathbf{w}_0 e^{\zeta t + i\mathbf{q}\cdot\mathbf{r}} \quad (54)$$

$$(55)$$

and separate the components of the velocities \mathbf{u} and \mathbf{w} into their longitudinal and transverse parts ($\nabla \times \mathbf{u} = 0$ and $\nabla \cdot \mathbf{u} = 0$, respectively, and similarly for \mathbf{w} .) Choosing \mathbf{q} along the z-axis, we rewrite

$$\zeta \delta\rho_0 + iq\rho_0 u_0^z = 0 \quad (56)$$

$$\zeta u_0^z + iq \frac{1}{\rho_0} \left(\frac{\partial P}{\partial \rho} \right)_c \delta\rho_0 + iq \frac{1}{\rho_0} \left(\frac{\partial P}{\partial c} \right)_\rho \delta c_0 + q^2 \frac{1}{\rho_0} \left(\frac{4}{3}\eta + \eta_b \right) u_0^z = 0 \quad (57)$$

$$\zeta u_0^{x(y)} + q^2 \frac{\eta}{\rho_0} u_0^{x(y)} = 0 \quad (58)$$

$$\zeta w_0^z + iq \left(\frac{\partial \mu_D}{\partial \rho} \right)_c \delta\rho_0 + iq \left(\frac{\partial \mu_D}{\partial c} \right)_\rho \delta c_0 + \gamma w_0^z = 0 \quad (59)$$

$$\zeta w_0^{x(y)} + \gamma w_0^{x(y)} = 0 \quad (60)$$

$$\zeta \delta c_0 + iq c_0 (1 - c_0) w_0^z = 0, \quad (61)$$

where the upper indexes indicate Cartesian components of the vectors. We define the kinematic longitudinal viscosity $\nu_l = (4\eta/3 + \eta_b)/\rho_0$ and the kinematic shear viscosity $\nu = \eta/\rho_0$. Since the model is isothermal there is no coupling to the heat modes and the transverse velocities are completely decoupled from the remaining variables. As a consequence, the two shear modes describing standard diffusion of transverse momentum, can be represented as

$$u^{x(y)}(\mathbf{r}, t) = u_0^{x(y)} e^{-\nu q^2 t + i\mathbf{q}\cdot\mathbf{r}} \quad (62)$$

Similarly, the transverse component of the field \mathbf{w} decays exponentially fast due to the presence of internal friction

$$w^{x(y)}(\mathbf{r}, t) = w_0^{x(y)} e^{-\gamma t + i\mathbf{q}\cdot\mathbf{r}}. \quad (63)$$

The remaining four longitudinal modes are mutually coupled and one has to consider the roots of the determinant

$$\begin{vmatrix} \zeta & iq\rho_0 & 0 & 0 \\ \frac{iq}{\rho_0}(\frac{\partial P}{\partial \rho})_c & \zeta + \nu_l q^2 & 0 & \frac{iq}{\rho_0}(\frac{\partial P}{\partial c})_\rho \\ iq(\frac{\partial \mu_D}{\partial \rho})_c & 0 & \zeta + \gamma & iq(\frac{\partial \mu_D}{\partial c})_\rho \\ 0 & 0 & iq c_0(1 - c_0) & \zeta \end{vmatrix}$$

For the hydrodynamic analysis, it is sufficient to compute the roots of the associated fourth order secular equation to order q^2 , so to obtain the following roots:

$$\zeta_{acoustic} = \pm i c_s q - \Gamma q^2 \quad (64)$$

with a sound velocity given by

$$c_s = \sqrt{(\frac{\partial P}{\partial \rho})_c} \quad (65)$$

and where

$$\Gamma = -\frac{1}{2} \left(\nu_l + (\frac{\partial \mu_D}{\partial \rho})_c (\frac{\partial P}{\partial c})_\rho / (\frac{\partial P}{\partial \rho})_c \right) \quad (66)$$

The last term in eq. (66) represents the damping of sound waves by interdiffusion of the two species. Finally the species diffusion is associated with the eigenvalue

$$\zeta_{diffusive} = -D_0 q^2 \quad (67)$$

with

$$D_0 \equiv \frac{1}{\gamma} c_0(1 - c_0) \frac{\partial \mu_D}{\partial c} \quad (68)$$

which should be compared with the r.h.s of eq.(44).

V. NUMERICAL VALIDATION

In this section we compare some of the theoretical predictions with the numerical results obtained by applying the Lattice Boltzmann numerical solution of the coupled kinetic equations (1). The discretized form of these equation has been presented in detail in appendix B of ref. [25] and will not be repeated here for the sake of brevity.

A. Molecular diffusion

We first determine the diffusion coefficient of an hard-sphere mixture at various packing fractions and compositions and then consider the effective diffusion coefficient for a system subject to a special type of shear flow. In the case of small perturbations around the equilibrium state, it is possible to obtain an analytical estimate of the so-called Taylor dispersion [32].

Let us first consider the relaxation of an initial concentration gradient in a system with $m^A = m^B$, $\mathbf{u} = 0$ and whose global density is uniform. In the initial state the composition varies along the z direction as a sinusoidal wave of small amplitude, Δ , and given by the two distribution functions

$$\begin{aligned} f^A(\mathbf{r}, \mathbf{v}, t=0) &= (n_0 + \Delta \sin(q_z z)) e^{-m\mathbf{v}^2/(2k_B T)} \\ f^B(\mathbf{r}, \mathbf{v}, t=0) &= (n_0 - \Delta \sin(q_z z)) e^{-m\mathbf{v}^2/(2k_B T)}. \end{aligned} \quad (69)$$

The diffusion constant is computed by monitoring the decay of a particular peak of n_A , which according to the theory, decreases exponentially with an inverse characteristic time $1/\tau(q_z) = D^{AB} q_z^2$. The extracted value of D^{AB} as a function of the packing fraction for several values of the bulk composition and different diameter ratios is reported in Fig. 2.

We observe that the mutual diffusion coefficient, D^{AB} , increases as the concentration of large spheres increases at fixed value of the packing fraction, according to the theoretical prediction eq.(43). On the other hand, at fixed concentration and high packing fractions, the diffusion constant decreases as a function of the packing fraction.

However, in the low density region we find the unexpected result that the diffusion constant increases with the packing fraction. This regime correlates with the fact that the decay of the perturbation (69) does not decay diffusively, but displays an oscillatory damped behavior.

This phenomenon occurs when the wavevector of the initial fluctuation is larger than a critical value $q_c = \sqrt{\gamma/4D}$. This apparent deviation from the standard diffusive behavior is the result of probing the system at small scales where standard hydrodynamics does not apply. However, since the phenomenon occurs only at finite wavelength below a certain threshold it is not in contradiction with the hydrodynamic picture presented above. The diffusion equation obtained in section IV A holds in the hydrodynamic regime when, as a

result of many collisions, the fluid has reached local equilibrium. In terms of wave-vector and frequency one requires $q\lambda_{mf} \ll 1$ and $\omega\tau \ll 1$, where λ_{mf} is the mean free path and τ the mean collision time. At densities typical of a liquid the mean free path is of the order of magnitude of the molecular size, while in a very diluted gas λ_{mf} becomes large so that the range of validity of hydrodynamic formulae shrinks.

The following simple analysis shows the origin of the non monotonic decay. We first decouple the “acoustic” modes in the hydrodynamic matrix, by neglecting the derivative of the pressure with respect to concentration, and consider the simplified equation (by neglecting $(\frac{\partial P}{\partial c})_\rho \simeq 0$):

$$\zeta^2 + \gamma\zeta + \Delta q^2 = 0 \quad (70)$$

with $\Delta = c_0(1 - c_0)(\frac{\partial \mu_D}{\partial c})_\rho$. The following decay frequencies:

$$\zeta_\pm = -\frac{\gamma}{2} \pm \sqrt{\frac{\gamma^2}{4} - \Delta q^2} \quad (71)$$

display oscillatory-damped behavior for concentration fluctuations of wave-vectors $q > q_c$, with $q_c = \sqrt{\frac{\gamma^2}{4\Delta}}$. At low density we can obtain an analytic expression for such a crossover, since $\Delta \simeq \frac{k_B T}{m}$ and

$$\gamma = \frac{8}{3} \frac{\sqrt{k_B T}}{\sqrt{2\pi m}} \frac{1}{\lambda_{mf}}, \quad (72)$$

where the mean free path is $\lambda_{mf} = \frac{1}{\sqrt{2}\pi g(\sigma)\sigma^2 n}$. In terms of the wavelength $L_c = 2\pi/q_c$ the transition from the diffusive to the oscillatory damped behavior occurs when the Knudsen number, expressing the ratio of the two characteristic lengths of the problem, is

$$Kn = \frac{\lambda_{mf}}{L_c} = \frac{4}{3} \frac{1}{(2\pi)^{3/2}} \simeq 0.08. \quad (73)$$

In other words, if the wavelength of the fluctuation is of the order of the mean free path, collisions are not frequent enough to restore local equilibrium, which is the mechanism determining molecular diffusion.

Such an oscillatory decay of diffusive modes should be contrasted with the behavior associated to a simple BGK collisional kernel, which does not have such oscillations [52–54]. In fact, in the latter the friction constant, γ , is not determined self-consistently but enters as a free parameter and is usually assumed to be a density independent quantity.

B. Taylor dispersion in a periodically modulated flow

In this subsection, we discuss a problem where one observes the interplay of a macroscopic and microscopic mechanisms. This occurs, for instance, when an inhomogeneous concentration field is subjected to a non-uniform macroscopic velocity flow. As discovered by Taylor such a situation determines an enhancement of the molecular diffusion in the direction of the flow, known as Taylor dispersion [32].

The theoretical calculation, sketchly reported hereafter for the sake of completeness, is based on a multiscale perturbation analysis. We refer to the work of [55] for mathematical details.

We consider a box of length L_x and cross-section $L_y \times L_z$ and a fluid velocity $u^x(y)$ periodically modulated along the y direction:

$$\mathbf{u}(\mathbf{r}) = \left(-U \cos\left(\frac{2\pi y}{L_y} + \pi\right), 0, 0 \right) \quad (74)$$

The boundary conditions are such that at the extremes of the box $u^x = -U$, and at the center of the box $u^x = U$.

In the diffusive regime the concentration obeys the three dimensional advection-diffusion equation (45) with \mathbf{u} given by (74). However, the description can be contracted, using multiscale techniques, and instead of studying the evolution of the full concentration field one can focus attention on the sectionally averaged concentration, $C(x, t)$ given by:

$$C(x, t) = \frac{1}{L_y} \int_0^{L_y} dy c(x, y, t) \quad (75)$$

in the presence of a laterally averaged velocity

$$U_0 = \frac{1}{L_y} \int_0^{L_y} dy u^x(y). \quad (76)$$

The theory [55] shows that the salient information about the diffusive process is given by the following simpler one-dimensional advection-diffusion equation:

$$\frac{\partial}{\partial t} C(x, t) + U_0 \frac{\partial}{\partial x} C(x, t) = D_{eff} \frac{\partial^2}{\partial x^2} C(x, t) \quad (77)$$

where the new coefficient D_{eff} is due to the renormalization of the standard molecular diffusion induced by the macroscopic velocity field $u^x(y)$. Its value is given by the formula:

$$D_{eff} = D^{AB} \left(1 + \frac{U^2 L_y^2}{8\pi^2 (D^{AB})^2} \right) = D^{AB} \left(1 + \frac{Pe^2}{2\pi^2} \right) \quad (78)$$

where the Peclet number, $Pe = UL_y/2D^{AB}$, is the ratio between the rate of advection and the rate of molecular diffusion.

So far goes the theory. The above scenario can be checked with a numerical calculation similar to that of sub-section V A appropriately modified in order to account for the presence of the field $\mathbf{u}(\mathbf{r})$. We assumed an initial concentration inhomogeneity along the x direction under the form of two initial density fields:

$$n^A(x) = n_0^A + \Delta \sin(k_x x)$$

$$n^B(x) = n_0^B - \Delta \sin(k_x x).$$

and verified that the homogeneous state is recovered exponentially with a characteristic time $1/\tau(q) = D_{eff}^{AB}q^2$, that depends on the strength of the applied velocity field and its wavelength as predicted by (78). In Figs. 3 and 4 we display the different stages of the evolution of the concentration field in the left columns and of the velocity field in the right columns, obtained from our LBM code, for two different values of the strength of the imposed velocity field. One can see that the concentration gradient tends to decrease as the time increases and so does the concentration current. In a matter of ~ 30 LBM timesteps the concentration gradient is barely visible and the currents have faded away. During its evolution, the density field initially distorts in a quasi-parabolic shape and subsequently in a v-shaped form, being more pronounced at high Peclet. The current displays non-trivial patterns alternating in time and position as time proceeds.

The numerical results obtained from our simulation are checked against theoretical predictions, derived under the assumption that the concentration field is assimilable to a passive scalar. Fig. 5 displays the relaxation time for a concentration inhomogeneity for various values of the Peclet number, and for two values of the packing fraction. The effective diffusion increases quadratically as a function of the Peclet number as predicted by the theory.

VI. CONCLUSIONS

Using a microscopic approach based on the multicomponent Boltzmann-Enskog equation and a self-consistent treatment of the interactions we have studied the diffusional properties of a mixture of hard-spheres. In order to obtain a working scheme we have employed a series of hypothesis and approximations. First, we have assumed that the complex many

body problem can be represented by means of a modified Boltzmann-Enskog equation, the RET, where only configurational two-particle correlations are accounted for. Since the RET requires a reasonable effort only in the case of hard-sphere interactions, the attractive potential tails have been treated within the RPA, an approximation which fails to accurately reproduce the transport coefficients. A second important simplification adopted is the method of Santos et al. [31], where the slowly varying, hydrodynamic fields and the fast non-hydrodynamic ones are decoupled at kinetic level, and the latter are treated in a simplified way. Third, we only considered isothermal situations for the sake of simplicity. The extension to non-isothermal systems will be the subject of future work. Finally, we have discretized the resulting transport equations on a lattice and employed the Lattice Boltzmann method to obtain numerical solutions.

The present method represents a valid alternative to popular mesoscopic techniques, such as the pseudo-potential-Lattice-Boltzmann (LB) method or free-energy based models (see for instance, ref. [19] and references therein), that retain the functional form of the equilibrium free energy, but sacrifice the possibility of determining the transport from the microscopic pair potentials through controlled approximations. In contrast, our approach leads in a quite natural fashion to the determination of thermodynamic forces compatible with the free energy methods, but in addition determines self-consistently the non equilibrium forces necessary to guarantee the correct hydrodynamic behavior.

We have obtained a derivation of the advection-diffusion equation for the concentration and the self-consistent determination of the diffusion coefficient, which in the homogeneous case reduces to the Chapman-Enskog value. The study of the long wavelength and low frequency properties of the model has been performed and agrees with the results obtained by standard hydrodynamic analysis [36, 56] of mixtures.

A second merit of the present formulation is to lend itself to numerical solution via the Lattice Boltzmann method. Our computational approach takes into account the dynamics of flowing liquids on space-time scales of hydrodynamic interest. These scales are out of reach for Molecular Dynamics, which in principle describes *ab-initio* the system, since the probabilistic nature of the singlet distribution function does not require averaging the data as in particle-based methods. In addition, the proposed method can cope very naturally with the critical situations of low concentrations of one species.

By simple numerical experiments, we have verified that the present version of the LBM

allows to extract the value of the diffusion coefficient from the decay of small periodic concentration fluctuations. Moreover, we considered cases where the Taylor dispersion mechanism provides an enhancement of diffusion, thus further showing that the present numerical scheme is capable of handling molecular mechanisms together with driving forces acting on much larger scales.

We plan future applications of the present approach to the study of non-uniform substrates, multiphase flows and transport in narrow channels.

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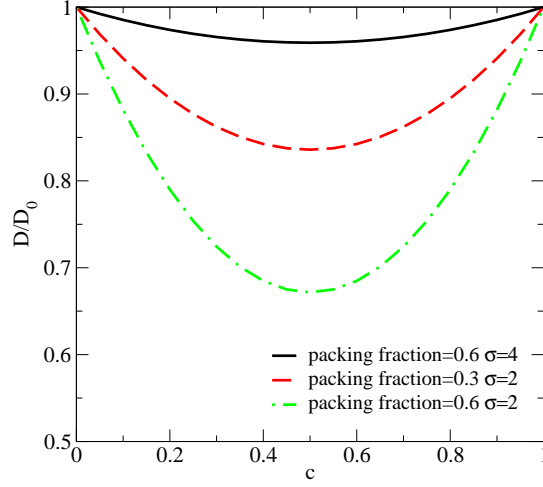


FIG. 1: Ratio between the mutual diffusion coefficient with attractive tails and the coefficient of a system without attractive tails as a function of concentration. The mixture consists of equisized spheres with attractive potentials whose strength is chosen according to the Lorentz-Berthelot mixing rule (46). The hard sphere radii are $\sigma_{AA} = \sigma_{BB} = 2$ in one case and $\sigma_{AA} = \sigma_{BB} = 4$ and the packing fraction $\xi_3 = \frac{\pi}{6}(n^A \sigma_{AA}^3 + n^B \sigma_{BB}^3)$ is kept fixed at values 0.6 and 0.3, while varying concentration. The effect of the potential tails is the largest for equal concentrations.

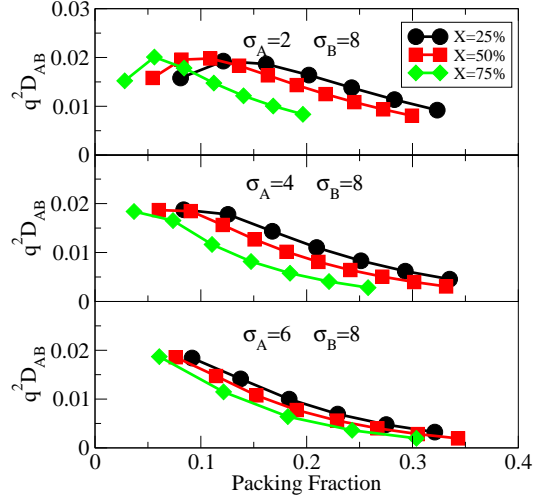


FIG. 2: Numerical test of the diffusion process in bulk conditions. The vertical axis represents a measure of the mutual diffusion coefficient obtained from LBM simulations (all data expressed in LBM timestep units). We monitored the evolution towards equilibrium of a sinusoidal concentration fluctuation (see eq. (69)) of wave-vector q_z and extracted the characteristic decay time, $1/\tau(q_z) = D^{AB}q_z^2$. The plots report the inverse decay time versus packing for various values of the composition and diameter ratio and for a fixed value of $q_z = 40$.

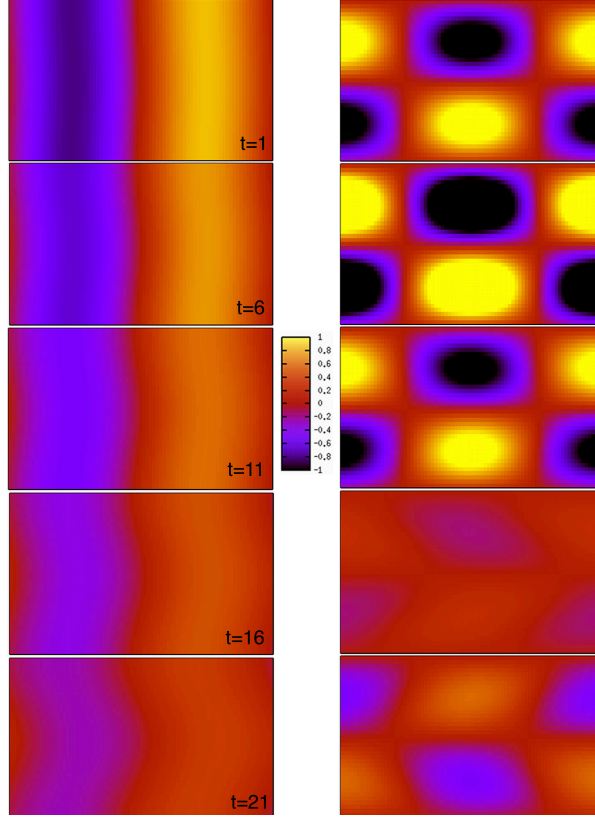


FIG. 3: Time evolution of the density (left column) and current (right column) in Taylor dispersion. The initial concentration modulation is along the x direction whereas the external field varies along the y direction according a cosine law. In the left column we report the evolution of the density of the large species every 5 LBM timesteps. In the right column we report the evolution of the associated current in the y direction. Data correspond to $\sigma_{AA} = 8$, $\sigma_{BB} = 4$, $c_0 = 0.5$, $Pe = 1$, average packing $\xi_3 = 0.211$, and for a simulation box of $80 \times 40 \times 40$. The color scale refers to both the density and current plots. Both reported data are normalized according to the initial values of the respective fields.

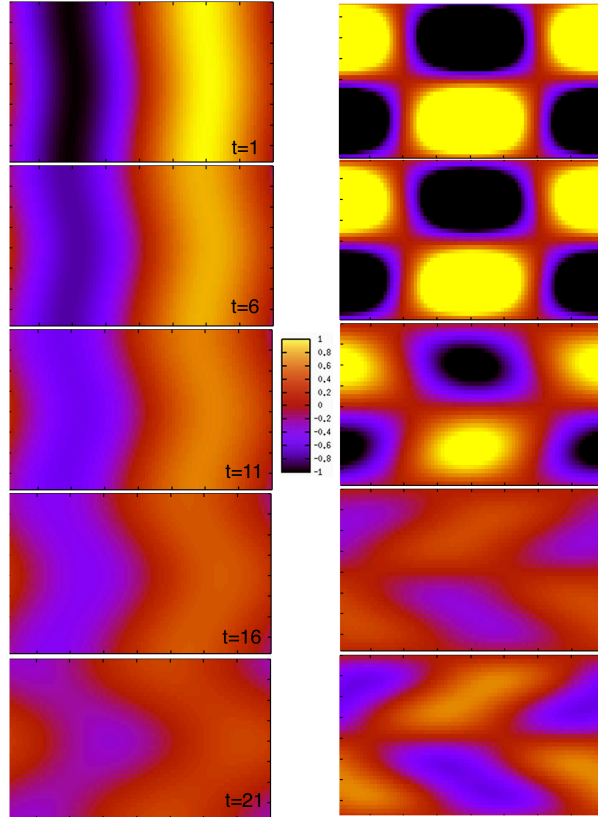


FIG. 4: Time evolution of the density (left) and current (right) in Taylor dispersion. The fluid parameters are the same as in Fig. 3, but for Peclet number $Pe = 5$.

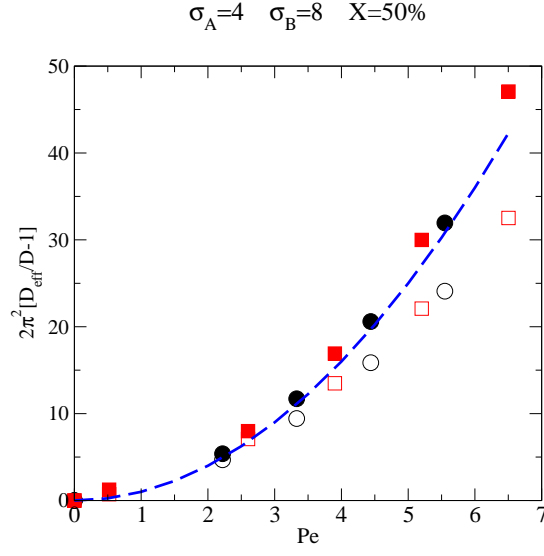


FIG. 5: Mutual diffusion coefficients in Taylor dispersion obtained for packing fraction of 0.211 (circles) and 0.332 (squares respectively). Filled symbols correspond to a box of length $L_x = 80$, while open symbols to a box of length $L_x = 40$. The dashed line corresponds to eq. (78).